The Polarisation of Raman Lines: Some Hydrocarbons.

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Abstract.

The results of a study of the polarisation characters of the Raman lines in benzene, cyclohexane and pentane are described. The lines with a frequency shift of 992 in benzene and 800 and 992 in cyclohexane are distinguished for their almost perfect polarisation. It is suggested that these represent inactive oscillations which is supported by the fact that the 992 of benzene appears only weakly and the 800 and 992 of cyclohexane not at all in the respective infra-red absorption curves. In all the three compounds, the different components of the characteristic hydrogen frequency appear with very different degrees of polarisation, the more intense components being usually the better polarised. Benzene is distinguished from the two other compounds by exhibiting several lines which show no detectable polarisation.

1. *Introduction.*

In an earlier paper [1] the author has described the results of a systematic investigation of the polarisation of lines in the Raman spectra of some simple compounds. The study at the time was however confined to such compounds as are marked by their simplicity of structure and certain striking similarities are shown to exist between the Raman lines arising from molecules having analogous structures. It is thought desirable to extend the investigations to at

[1] Ind. Jour. Phys., 5, 59 (1930).

least some typical compounds chosen from the very vast field of organic chemistry and particularly to those Raman lines which have been given a definite origin. It is well known that these compounds give very complicated Raman spectra the interpretation of which is still very obscure even in relatively simple cases like benzene. Extensive investigations by Venkateswaran, Dadieu and Kohlrausch and others have shown that a study of the Raman spectra affords a powerful means of elucidating various points which are of interest to the structural chemist. One of the most fascinating phenomena is that certain lines, whiie preserving their individuality, undergo remarkable variations of intensity and position as we pass from compound to compound in any particular group or from one well defined chemical group to another. There has been however very little work done so far from the view point of polarisation. In the present paper three typical liquids, *viz.*, benzene and pentane representing the aromatic and the aliphatic classes of compounds respectively and cyclohexane, a transition between them, have been chosen and an investigation made of the polarisation characters of their Raman spectra.

2. *Experimental arrangements.*

All the three liquids were of Kahlbaum's make and have been repurified by slow distillation in vacuum. The liquids were contained in large double bulbs and illuminated by the light of a mercury arc lamp focussed on them by means of a powerful glass condenser. For liquids which are available in large quantities such an illumination affords an ideal arrangement in which the reflected light is almost completely eliminated. All the polarisation pictures were taken without the use of any lens in the path of the scattered light. A large two prism glass spectrograph supplied by Adam Hilger is made use of in the investigation. The details of the method and the corrections employed are the same as those described by the author in his earlier paper.

3. *Polarisation of the Raman lines.*

The results obtained with the three liquids are given in Table I. I represents the relative intensity of the line and ρ the depolarisation defined as the ratio of the weaker to the stronger component in the scattered light observed normal to the direction of the primary beam. The spectrograms are not very intense and show only the more prominent lines. With well polarised weaker lines and almost completely polarised strong lines the weak component is either seen very feebly or not at all in which case an upper limit for the depolarisation factor is given.

TABLE I.

Polarisation of Raman lines

Benzene	ν	607	852	992	1181	1597	3046	3060		
	I	8	5	10	5	5	3	10		
	ρ	1	1	<0·05	—	1	1	0·85		
Cyclohexane	ν	800	992	1028	1268	1445	2853	2890	2921	2937
	I	4	2	2	2	2	8	2	4	8
	ρ	0·1	<0·15	0·3	0·4	0·5	0·13	<0·5	0·5	0·1
Pentane	ν	402	764	843	867	1454	2857	2873	2915	2936	2962
	I	2	1	2	1	3	3	5	3	4	3
	ρ	<0.5	<0.5	<0·5	<0·5	0·3	0·7	0·22	0·7	0·5	0·75

The results with benzene are in fair agreement with those already reported by Cabannes.[2] The case of 1181 is interesting as it happens to show apparently quite different degrees of polarisation according as it is excited by 4046 or 4358; in the former case it is well polarised, the depolarisation being at the most only about 20% whereas in the latter it is almost unpolarised. Such an anomaly arises from the fact that in the former case the well polarised principal line 990 arising from

[2] Trans. Farad. Soc., 25, 813 (1929).

4077 falls on the top of it and gives it an appearance of a highly polarised line whereas in the latter the line 2946 from 4046 falls on the top of it and gives it the appearance of complete depolarisation. The 990 line is however much more intense than this frequency and it is almost certain that the high polarisation in the former case is largely due to its presence. On the other hand the one corresponding to 2946 is perhaps comparable in intensity with 1181 and the results seem to suggest that both these lines are more or less completely unpolarised. The two close lines at 3046 and 3060 are of special interest as they both arise from hydrogen and are quite differently polarised. The value given by Cabannes differs from either and is midway between the two, a result which may probably be attributed to a superposed effect. The extraordinary intensity of the 990 and 3060 lines and their high degree of polarisation as a contrast to all other lines may be noted.

Polarisation results with cyclohexane and pentane are new and reported here for the first time.

4. *Comparison of the liquids.*

Carbon oscillations.—In the first instance it may be noted that in cyclohexane and pentane most of the Raman lines are well polarised, lines showing large imperfections of polarisation being entirely absent whereas in benzene all lines except 992 and 3060 are more or less completely unpolarised. This outstanding feature of the polarisation of Raman scattering has an analogy in Rayleigh scattering in that the unmodified light scattered by the aliphatic group of compounds shows very little imperfection of polarisation whereas it is largely depolarised in the group of aromatic compounds.

The line of extraordinary prominence in benzene is the one at about 992 which continues to appear in almost all its derivatives in a slightly shifted position, *viz.*, 1000. Remarkable variations in intensity exhibited by this line with increasing complexity of substitution have been discussed in

a recent paper by Venkateswaran and Bhagavantam.[3] Its great intensity suggests that it is an inactive oscillation probably corresponding to a symmetric motion of alternate carbon atoms.[4] The curves showing the infra-red absorption of benzene given by Coblentz, Bell and others show only a feeble absorption corresponding to this frequency although there is a prominent absorption maximum in its neighbourhood. The almost complete polarisation of this line is in agreement with such a view and the results already deduced by the author in his previous paper regarding symmetrical oscillations. A study of its polarisation in various derivatives will be of great interest.

When we pass to cyclohexane the line has not changed either in position or in the state of polarisation appreciably, a result which is of great significance as it suggests essentially a similar hexagonal symmetry for the latter molecule also. This is further supported by the fact that as in benzene, this oscillation is inactive in cyclohexane as well and does not give rise to any corresponding absorption in the infra-red region.[5] The only other prominent frequency in cyclohexane, besides those attributable to hydrogen, is the one at 800 and is also not represented by any maximum in the infra-red absorption. This fact as well as its large intensity and polarisation, both suggest that it corresponds to a symmetric distortion of the molecule involving no change in the electric moment. It may be mentioned that both 800 and 992 resemble each other further in that they both are very sharp unlike the other lines in the spectrum. Such a close similarity which the 800 line bears to 992 suggests that both of them probably represent the same oscillation: in the case of 992 carbon atoms alone oscillate whereas a simultaneous disturbance of the attached hydrogen atoms which are more important here than in benzene, will account for the slightly lower value 800 for the second oscillation.

[3] Proc. Roy. Soc., 128, 252 (1930).

[4] This point is dealt with more fully in another paper by the author.

[5] J. Lecomte, Le Spectre Infrarouge, 217 (1928)

The situation in pentane is however quite different as there exists in the place of this unique oscillation, a series of oscillations 402, 764, 843 and 867 all of comparble intensity and polarisation characters. The chemical analogue of this feature is the distribution of carbon atoms along a zig zag chain in the one case and at the corners of a hexagonal ring in the other.

Hydrogen oscillations.—The lines 1597, 3046, 3060 in benzene; 1445, 2853, 2890, 2921, 2937 in cyclohexane and 1454, 2857, 2873, 2915, 2936, 2962 in pentane have all been attributed to oscillations of the hydrogen atoms by various investigators. It is interesting to note that the intensity and polarisation characters exhibited by this series constitute a very wide range: there are lines of extreme feebleness as well as high intensity and lines showing high degree of polarisation as well as a large imperfection of polarisation. The origin of such a multiplicity of hydrogen frequencies is not clear at present although in a general way it may be connected with the lightness of the atom and the consequent ease with which it is affected by the environment. There is however no explanation which satisfactorily accounts for the observed multitude of frequencies. It appears reasonable to suppose that the origin of such a multiplicity will also account, if properly located, for the remarkable polarisation and intensity characters. It must however be mentioned here that usually high intensity and large polarisation go together.

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